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Copolymerization of Ethylene with α-Olefins Containing Various Substituents Catalyzed by Half-Titanocenes: Factors Affecting the Monomer Reactivities

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ABSTRACT: Ethylene copolymerizations with various pentenes [1-pentene, 4-methyl-1-pentene (4M1P), 3-methyl-1-pentene (3M1P), 4,4-dimethyl-1-pentene (NHEP)] using Cp*TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (**1**), CpTiCl$_2$(N═C^{t}Bu$_2$) (**2**), [Me$_2$Si(C$_5$Me$_4$)(N^{t}Bu)]TiCl$_2$ (**4**) − MAO catalyst systems have been explored. Both **1** and **2** exhibited high catalytic activities affording high molecular weight copolymers with unimodal molecular weight distributions; the $r_E r_C$ values ($r_E = k_{EE}/k_{EC}$; E = ethylene; C = comonomer) by **1** were small, suggesting that the monomer incorporations were rather alternating, whereas the copolymerization by **4** proceeded in a random manner ($r_E r_C$ = ca. 1) except the copolymerization with 3M1P. **1** exhibited remarkable both catalytic activities and 3M1P incorporation in the ethylene/3M1P copolymerization, and the r_E value (8.73) was much smaller than that by **4** (92), **2** (28.3). Both **1** and **4** showed better NHEP incorporations than **2** in the ethylene/NHEP copolymerization, and the rather large r_E value by **2** (6.77) compared to those by **1** (2.58−2.94) was also obtained in the copolymerization with 4M1P. These results clearly indicate that the monomer reactivities (r_E values) are influenced not only by the substituent in the olefins, but also by the nature of the catalytically active species (structure, and ligand set employed). Both **1** and **2** also exhibited notable catalytic activities in the copolymerization of ethylene with 1-dodecene, 1-hexadecene, affording high molecular weight copolymers with unimodal molecular weight distributions. No notable differences toward the r_E values by **1**,**2**,**4** were seen, although the values were slightly affected by both the steric bulk of olefins (linear branching) and the catalyst structure employed.

Introduction

Polyolefins are important commercial synthetic polymers, and the market capacity is still increasing even in the conventional polyolefins such as polyethylene (HDPE, LLDPE), polypropylene (PP). Considerable attention has been paid to the research subjects for synthesis of new polyolefins with specified functions, and precise control in the copolymerization is thus an important method that usually allows the alteration of the (physical, mechanical, and electronic) properties by varying the ratio of individual components. It has thus been believed that design of the efficient transition metal complex catalysts should be the key for the success, and recent progress in the newly designed catalysts offers a new possibility.[1−8]

Generally, structural features of the catalyst, in particular the steric bulk of ligand, bite angle, configuration and conformation, influence the coordination and/or insertion of monomers in transition metal catalyzed coordination polymerization reactions,[9,10] and this is an distinct difference from conventional radical and ionic polymerization reactions. It has been known that ethylene/α-olefin copolymerization, especially by metallocene-type catalyst, generally proceeds in a random manner and the monomer sequences obey the first order Markov model.[9,10] As exemplified in Table 1,[8,10,11,12] the efficiencies in the ethylene copolymerizations can be evaluated by the monomer reactivity ratio (r_E), which is defined as $r_E = k_{EE}/k_{EC}$ (E = ethylene, C = comonomer), and the r_E values decreases in the order: Cp$_2$ZrCl$_2$ ≫ *rac*-Me$_2$Si[benz(e)Ind]$_2$ZrCl$_2$ > [Me$_2$Si(C$_5$Me$_4$)(N^{t}Bu)]TiCl$_2$ (CGC). It is also known that the r_E values by ordinary metallocenes were dependent upon the polymerization temperature, whereas the $r_E r_C$ ($r_E r_O$) values were ca. 1.0, indicating that the copolymerizations proceed in a random manner (or comonomer incorporations are random).[2,3] The facts would support an assumption that *bridge constrains more open coordination sphere for bulky* α*-olefins*,[2,3] although the coordination sphere should not be the exclusive factor for better comonomer incorporation based on recent reports.[13]

Nonbridged half-metallocenes of the type, Cp′M(L)X$_2$ (Cp′ = cyclopentadienyl group; M = Ti, Zr, Hf; L = anionic donor ligand such as OAr, NR$_2$, N═CR$_2$, N═PR$_3$, etc.; X = halogen, alkyl), have been considered as promising candidates for the new efficient catalysts,[8,14−16] because these complex catalysts display unique characteristics for synthesis of new polymers[8,12,14,17−24] that are not prepared (or very difficult to be prepared) by ordinary catalysts such as Ziegler−Natta, metallocenes,[2] 'constrained geometry' type catalysts (CGC).[3] As exemplified in Table 1, the r_E values by Cp*TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (**1**) in ethylene/1-octene copolymerization (r_E = 2.65−2.9) are smaller than that by ordinary metallocenes, CGC (r_E = 4.1), and the values were not dependent upon the polymerization temperature employed.[11,11]

We already demonstrated that the half-titanocenes containing aryloxo, ketimide ligands display promising characteristics especially for copolymerization of ethylene with vinylcyclohexane,[18] 2-methyl-1-pentene,[12] styrene,[19] and with cyclic olefins.[14,20−22] It turned out that an efficient catalyst for the desired (co) polymerization can be modified by simple replacement of both

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Table 1. Typical r_E and r_O Values in Ethylene/1-Octene Copolymerization Using Various Group 4 Transition Metal Complex Catalysts[a]

complexes	temp/°C	r_E	r_O	r_Er_O
Cp_2ZrCl_2[b]	40	32.8	0.05	1.17
rac-$Me_2Si(Ind)_2ZrCl_2$[b]	40	18.9	0.014	0.27
rac-$Me_2Si(Benz[e]Ind)_2ZrCl_2$[b]	40	10.7	0.076	0.81
rac-$Me_2Si(2\text{-}MeBenz[e]Ind)_2ZrCl_2$[b]	40	10.1	0.118	1.2
rac-$Me_2Si(2\text{-}MeBenz[e]Ind)_2ZrCl_2$[c]	40	8.16	0.14	1.14
$[Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$[b]	40	4.1	0.29	1.19
$Cp^*TiCl_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ (**1**)[d]	40	2.65	0.09	0.23
$Cp^*TiCl_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ (**1**)[e]	25	2.9	0.12	0.34
rac-$Me_2Si(2\text{-}MeBenz[e]Ind)_2ZrCl_2$[c]	0	4.71	0.22	1.06
rac-$Me_2Si(2\text{-}MeBenz[e]Ind)_2ZrCl_2$[c]	20	6.45	0.18	1.14
rac-$Me_2Si(2\text{-}MeBenz[e]Ind)_2ZrCl_2$[c]	40	8.16	0.14	1.14
rac-$Me_2Si(2\text{-}MeBenz[e]Ind)_2ZrCl_2$[c]	60	10.61	0.1	1.11

[a] Conditions: in toluene, $r_Er_O = 4[EE][OO]/[EO]^2$ (E = ethylene, O = 1-octene), $r_E = k_{EE}/k_{EO} = [O]_0/[E]_0 \times 2[EE]/[EO+OE]$, $r_O = k_{OO}/k_{OE} = [E]_0/[O]_0 \times 2[OO]/[EO + OE]$ ($[E]_0$, $[O]_0$: Initial monomer concentration). [b] Cited from ref 10c. [c] Cited from ref 10a. [d] Cited from ref 11b. [e] Cited from ref 12b.

the cyclopentadienyl fragment (Cp′) and the anionic ancillary donor ligands (L).[8b] More recently, we also demonstrated that these catalysts are also effective for introduction of functional groups into polyolefins in efficient manners.[14,23,24] As described above, structural features of the catalyst strongly influence the coordination and/or insertion of monomers in the coordination polymerization, however, there are no detailed studies for the ethylene copolymerizations with α-olefins containing various substituents, especially evaluation of r_E values in the copolymerization including effect of steric bulk in monomers and of structures in catalysts (including ligand effect). Since our half-titanocenes efficiently incorporate bulky α-olefins with high catalytic activities,[12,18,20−22] we thus explored the ethylene copolymerization studies with a series of α-olefins [such as 1-pentene, 4-methyl-1-pentene, 3-methyl-1-pentene, 4,4-dimethyl-1-pentene, 3,3-dimethyl-1-butene, 1-dodecene, 1-hexadecene] using various half-titanocenes (Scheme 1).[25−27] Through this research, we explored to obtain an important information for designing more efficient catalysts for copolymerization of ethylene with sterically bulky comonomers.

Results and Discussion

1. Copolymerizations of Ethylene with Substituted Pentenes by Various Half-Titanocenes−MAO Catalyst Systems.

1 1. Copolymerization of Ethylene with 1-Pentene (PEN) and 4-Methyl-1-pentene (4M1P) Using Cp′TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$), CpTiCl$_2$(N=C^{t}Bu$_2$)−MAO Catalyst Systems. $Cp^*TiCl_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ (**1**) and $CpTiCl_2(N{=}C^tBu_2)$ (**2**) have been chosen in this study, because **1** showed both remarkable catalytic activities and efficient comonomer incorporations in the copolymerizations of ethylene with 1-hexene,[11a] 1-octene,[11,11] and with 2-methyl-1-pentene;[12] **2** also showed both remarkable activity and efficient norbornene incorporation in the ethylene/norbornene copolymerization.[20c] $(^tBuC_5H_4)TiCl_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ (**3**), and $[Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$ (CGC, **4**), have also been chosen for comparison. These copolymerizations were conducted in toluene at 25 °C, and MAO white solid [prepared by removing toluene and $AlMe_3$ from commercially available MAO (PMAO-S, Tosoh Finechem Co.)] was chosen as the cocatalyst, because it was effective in the preparation of high molecular weight ethylene/1-butene copolymers with unimodal molecular weight distributions when **1** and **4** were used as the catalyst precursors.[17b]

Table 2 summarizes results for the copolymerization of ethylene with 1-pentene (PEN), 4-methyl-1-pentene (4M1P) using (**1**−**3**)−MAO catalyst systems varying the Al/Ti molar ratios.[28,29] As expected from the previous results in the ethylene/1-hexene copolymerization,[11] both **1** and **2** exhibited remarkable catalytic activities affording high molecular weight copolymers with unimodal molecular weight distributions in all cases. The activities by **1** were dependent upon the Al/Ti molar ratios employed, and the activity markedly increased at higher ethylene pressure and decreased upon increasing comonomer concentration (PEN, 4M1P, runs 6 and 13). As seen in the copolymerization with 1-hexene[11,11] as well as with 2-methyl-1-pentene,[12b] the M_n values in the resultant copolymers were not affected by the Al/Ti molar ratios but decreased upon increasing the comonomer contents. These results suggest that the dominant chain-transfer reaction in these copolymerizations by **1** would be either β-H elimination or β-H transfer to comonomer, not the chain transfer to Al. The activities in these copolymerizations by **2** were also dependent upon the Al/Ti molar ratios employed and the M_n values in the resultant copolymers were somewhat sensitive to both the Al/Ti molar ratios and the comonomer contents. As seen in the ethylene/1-hexene copolymerization,[11] **2** showed less efficient PEN incorporation than **1**, whereas the M_n values in the resultant poly(ethylene-*co*-PEN)s prepared by **2** were higher than those prepared by **1** [$M_n = 1.85 \times 10^5$ (run 2, PEN 36.5 mol % by **1**) vs 6.02×10^5 (run 17, PEN 37.6 mol % by **2**)]. Interestingly, 4M1P incorporations by **2** were less efficient than those by **1** [4M1P content 31.4 mol % (by **1**, run 9) vs 21.6 mol % (by **2**, run 20); ethylene 6 atm, 4M1P 1.32 M], although the copolymerization proceeded with remarkable catalytic activity affording high molecular weight poly(ethylene-*co*-4M1P)s with unimodal molecular weight distributions. As also reported previously in the ethylene/1-hexene copolymerization,[11,11] the $^tBuC_5H_4$−aryloxo analogue (**3**) showed better comonomer incorporations than the Cp*−aryloxo analogue (**1**), and these copolymerizations proceeded with moderate catalytic activities; the M_n values in the resultant copolymers by **3** were lower than those prepared by **1**,**2**.

Scheme 1

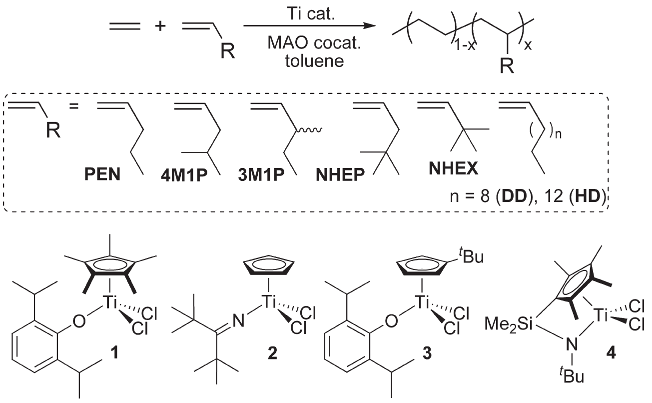


Table 3 summarizes monomer sequence (triad and dyad) distributions estimated on the basis of ^{13}C NMR spectra of poly(ethylene-*co*-PEN)s, poly(ethylene-*co*-4M1P)s.[28] As reported previously,[11,11] the resultant copolymers prepared by **1** possessed relatively higher percentage of ECE and CEC, and EC + CE sequences (E = ethylene, C = comonomer such as PEN, 4M1P) and the r_Er_C values by **1** calculated from the dyads were small (0.29−0.30), whereas, as shown in Table 1, r_Er_O values by ordinary metallocenes (Cp_2ZrCl_2 etc.) and CGC (**4**) in the ethylene/α-olefin copolymerizations were generally ca. 1.0,[10] clearly indicating that the

Table 2. Copolymerizations of Ethylene with 1-Pentene (PEN) and 4-Methyl-1-pentene (4M1P) by Cp*TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) [Cp* = C$_5$Me$_5$ (1)], CpTiCl$_2$(N=C^{t}Bu$_2$) (2), (^{t}BuC$_5$H$_4$)TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (3) Catalyst Systems with MAO[a]

run	complex (amount/μmol)	MAO/mmol	ethylene/atm	comonomer (concn/M)	yield/mg	activity[b]	M_n[c] × 10^{-4}	M_w/M_n[c]	content[d] /mol %
1	**1** (0.02)	1.5	6	PEN (1.52)	293	88000	17.3	1.97	
2	**1** (0.02)	3.0	6	PEN (1.52)	348	104000	18.5	1.90	36.5
3	**1** (0.02)	4.5	6	PEN (1.52)	310	93000	19.5	1.87	
4	**1** (0.02)	3.0	4	PEN (1.52)	162	48600	15.0	1.93	44.8
5	**1** (0.01)	3.0	8	PEN (1.52)	162	162000	24.0	1.97	31.2
6	**1** (0.02)	3.0	6	PEN (3.05)	285	85500	18.6	2.03	48.1
7	**1** (0.02)	1.5	6	4M1P (1.32)	314	95200	22.5	1.99	30.6
8[e]	**1** (0.02)	1.5	6	4M1P (1.32)	318	95400	22.9	2.14	
9	**1** (0.02)	3.0	6	4M1P (1.32)	278	83400	23.3	1.94	31.4
10	**1** (0.02)	4.5	6	4M1P (1.32)	276	82800	21.7	2.05	
11	**1** (0.02)	3.0	4	4M1P (1.32)	113	33900	18.6	2.09	39.6
12[f]	**1** (0.01)	3.0	8	4M1P (1.32)	175	175000	25.5	1.99	24.2
13	**1** (0.02)	3.0	6	4M1P (2.64)	206	61800	23.2	1.95	44.0
14	**2** (0.01)	1.5	6	PEN (1.52)	176	106000	81.7	1.93	
15	**2** (0.01)	3.0	6	PEN (1.52)	196	118000	72.3	1.91	29.1
16	**2** (0.01)	4.5	6	PEN (1.52)	181	109000	72.2	1.94	
17	**2** (0.01)	3.0	4	PEN (1.52)	174	104000	60.2	1.95	37.6
18	**2** (0.01)	3.0	6	PEN (3.05)	290	174000	63.2	1.96	41.6
19	**2** (0.01)	1.5	6	4M1P (1.32)	155	93000	50.6	1.97	
20	**2** (0.01)	3.0	6	4M1P (1.32)	162	97200	81.2	1.99	21.6
21	**2** (0.01)	4.5	6	4M1P (1.32)	146	87600	64.1	1.97	
22	**3** (0.05)	1.5	6	PEN (1.52)	183	22000	8.88	2.14	
23	**3** (0.05)	3.0	6	PEN (1.52)	208	25000	8.35	2.07	41.1
24	**3** (0.05)	4.5	6	PEN (1.52)	197	23600	8.98	2.00	
25	**3** (0.10)	1.5	6	4M1P (1.32)	209	12500	7.19	2.14	
26	**3** (0.10)	3.0	6	4M1P (1.32)	276	16600	7.47	2.17	37.1
27	**3** (0.10)	4.5	6	4M1P (1.32)	271	16200	7.56	2.09	

[a] Conditions: toluene and PEN or 4M1P total 30 mL, d-MAO (prepared by removing toluene and AlMe$_3$ from ordinary MAO), 25 °C, 10 min. [b] Activity = kg-polymer/mol-Ti·h. [c] GPC data in *o*-dichlorobenzene vs polystyrene standards. [d] Comonomer contents estimated by ^{13}C NMR spectra. [e] Additional independent polymerization run for run 7 to check the reproducibility. [f] 6 min.

Table 3. Monomer Sequence Distributions of Poly(ethylene-*co*-1-pentene)s and Poly(ethylene-*co*-4-methyl-1-pentene)s Prepared by Cp*TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) [Cp* = C$_5$Me$_5$ (1)], CpTiCl$_2$(N=C^{t}Bu$_2$) (2), (^{t}BuC$_5$H$_4$)TiCl$_2$(O-2,6-^{i}Pr2C$_6$H$_3$) (3) Catalyst Systems with MAO[a]

					triad sequence distribution[d] (%)						dyads[e] (%)						
run	catal	comonomer PEN or 4M1P	[comonomer]/ [E][b]	comonomer[c] content/mol %	EEE	EEC + CEE	CEC	ECE	CCE + ECC	CCC	EE	EC + CE	CC	r_E[f]	r_C[f]	r_Er_C[g]	ρ[h]
5	**1**	PEN	1.57	31.2	26.3	31.8	10.2	23.4	7.4	0.9	42.3	53.1	4.6	2.50	0.11	0.27	0.81
2	**1**	PEN	2.09	36.5	18.1	31.7	13.5	24.5	10.3	1.9	34.0	59.0	7.0	2.41	0.11	0.28	0.79
4	**1**	PEN	3.14	44.8	10.1	26.4	19.0	24.7	14.0	5.8	23.3	64.0	12.8	2.29	0.13	0.29	0.77
6	**1**	PEN	4.20	48.1	7.5	24.2	19.8	23.5	18.2	6.8	19.6	64.5	15.9	2.55	0.12	0.30	0.77
12	**1**	4M1P	1.36	24.2	44.6	11.8	19.4	18.7	5.5	trace	50.5	46.8	2.7	2.94	0.09	0.25	0.78
9	**1**	4M1P	1.81	31.4	36.7	8.7	23.2	22.7	7.7	1.0	41.0	54.1	4.9	2.75	0.10	0.27	0.80
11	**1**	4M1P	2.72	39.6	27.1	4.9	28.4	24.8	12.9	1.9	29.5	62.2	8.3	2.58	0.10	0.25	0.77
13	**1**	4M1P	3.62	44.0	23.5	trace	32.5	24.0	15.8	4.2	23.5	64.4	12.1	2.65	0.10	0.27	0.77
15	**2**	PEN	2.09	29.1	31.7	29.5	9.3	22.5	5.0	2.0	46.4	49.0	4.6	3.97	0.09	0.35	0.84
17	**2**	PEN	3.14	37.6	18.9	29.3	13.9	25.3	7.6	5.0	33.6	57.6	8.8	3.67	0.10	0.36	0.81
18	**2**	PEN	4.20	41.6	15.0	26.9	15.7	25.2	11.0	6.2	28.5	59.8	11.7	3.99	0.09	0.37	0.81
20	**2**	4M1P	1.81	21.6	55.5	4.8	20.7	12.9	5.3	0.8	63.0	33.7	3.3	6.77	0.11	0.73	1.01
23	**3**	PEN	1.09	41.1	14.8	29.2	13.7	24.6	12.2	5.5	29.4	59.0	11.6	2.09	0.19	0.39	0.82
26	**3**	4M1P	1.81	37.1	29.1	13.4	20.3	21.0	13.1	3.1	58.9	54.5	9.6	2.38	0.19	0.46	0.86

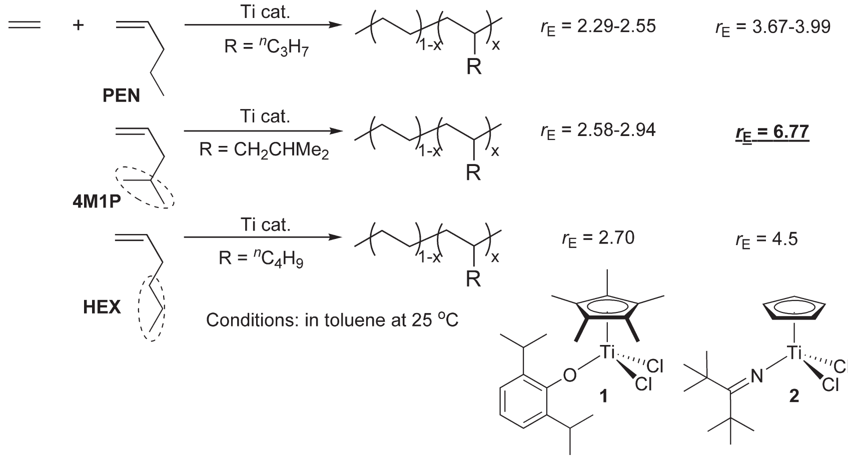
[a] Detailed polymerization conditions, see Table 2, *C* = comonomer [1-pentene (PEN) or 4-methyl-1-pentene (4M1P)]. [b] Initial molar ratio of [1-penetene (PEN) or 4-methyl-1-pentene (4M1P)]/[ethylene] in the reaction mixture. [c] Comonomer contents in the copolymer estimated by ^{13}C NMR spectra. [d] Calculated by ^{13}C NMR spectra, E = ethylene, C = comonomer [1-pentene (PEN) or 4-methyl-1-pentene (4M1P)]. [e] [EE] = [EEE] + $^1/_2$[EEC + CEE], [EC] = [CEC] + [ECE] + $^1/_2${[EEC + CEE] + [CCE + ECC]}, [CC] = [CCC] + $^1/_2$[CCE + ECC]. [f] r_E = $[C]_0/[E]_0 \times 2[EE]/[EC + CE]$, r_C = $[E]_0/[C]_0 \times 2[CC]/[EC + CE]$. [g] $r_Er_C = 4[EE][CC]/[EC + CE]^2$. [h] $\rho = 2[E][C]/[EC]$.

copolymerization proceeds in a random manner (comonomer incorporations are random). The r_Er_C values by the ^{t}BuC$_5$H$_4$-aryloxo analogue (**3**) were also small as seen in the ethylene/1-hexene copolymerization,[11,11] and the r_E values by **3** [r_E = 2.09 (run 23, PEN), 2.38 (run 24, 4M1P)] were smaller than those by **1** [r_E = 2.29−2.50 (PEN), 2.58−2.94 (4M1P)], suggesting that **3** showed better comonomer incorporations than **1**. The r_E values by the Cp-ketimide analogue (**2**) in these copolymerizations were larger than those by **1**, as seen in the ethylene/1-hexene copolymerization,[11c] suggesting that **2** showed less efficient comonomer incorporation than **1**; the r_Er_C values by **2** in the ethylene/PEN copolymerizations were also rather small (0.35−0.37). The ρ values (persistence ratios) by **1-3** in these copolymerizations were 0.77−0.86, and the values were somewhat smaller than 1 (random copolymerization) and no significant differences were seen except the copolymerization with 4M1P by **2**, as described below.

It should be noted that the r_E value by the Cp−ketimide analogue (**2**) in the ethylene/4M1P copolymerization was larger (6.77) than those by the Cp*−aryloxo (**1**) and the ^{t}BuC$_5$H$_4$−aryloxo (**2**) analogues (2.38−2.94) as well as those by **2** in the ethylene/1-pentene copolymerization (3.67−3.99), as summarized in Scheme 2. In contrast, the r_E values by **1** in the ethylene/4M1P copolymerization (2.58−2.94) were slightly larger than those in the ethylene/PEN copolymerization (2.29−2.55). The r_Er_C value, the ρ value were 0.73, 1.01, respectively (run 20), suggesting that the comonomer incorporation in the copolymerization was random. These results strongly suggest that the r_E values are influenced not only by the steric bulk of substituent in α-olefin (R in $CH_2{=}CHR$), but also by the structure of the catalytically active species; the r_E value by **2** was strongly affected by the methyl group in δ-position (Scheme 2). As proposed previously,[11,11] one probable, plausible explanation for a high level of comonomer incorporation by **1** would be due to the flexible internal rotation of both cyclopentadienyl and aryloxo ligands (Scheme 3),[30] and the reason for small r_Er_C values by **1** may also be explained as the result of internal rotation especially of aryloxide group which would form high percentage of favored conformation depending upon insertion of the previous monomer.[11b]

1.2. Copolymerization of Ethylene with 3-Methyl-1-pentene and 4,4-Dimethyl-1-pentene Using $Cp^*TiCl_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$, $CpTiCl_2(N{=}C^tBu_2)$, and $[Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$ Catalyst Systems with MAO. Table 4 summarizes results for the ethylene copolymerizations with 3-methyl-1-pentene (3M1P, mixture of *R* and *S*), 4,4-dimethyl-1-pentene (NHEP), and 3,3-dimethyl-1-butene (NHEX, *tert*-butyl ethylene) using $Cp^*TiCl_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ (**1**), $CpTiCl_2(N{=}C^tBu_2)$ (**2**), and $[Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$ (CGC, **4**) catalyst systems with MAO.[28] The Cp*−aryloxo analogue (**1**) exhibited high catalytic activities for the ethylene/3M1P copolymerization, affording high molecular weight copolymers with unimodal molecular weight distributions (runs 28,29), although the observed activities were somewhat lower than those in the copolymerizations with 4M1P, 1-hexene (HEX). The copolymerization with NHEP by **1** also proceeded with a moderate catalytic activity affording the copolymer with rather high NHEP content (run 31), whereas the copolymerization with NHEX under the similar conditions (ethylene 6 atm, NHEX 5 mL and toluene 25 mL) afforded polymer containing negligible amount of NHEX (run 32), as reported previously.[24b] The NHEP incorporation by **1** were more efficient than the 3M1P incorporation under the similar conditions (run 28 vs run 31, Table 4), as described below. The ethylene copolymerization with 3M1P,

Scheme 2



Scheme 3

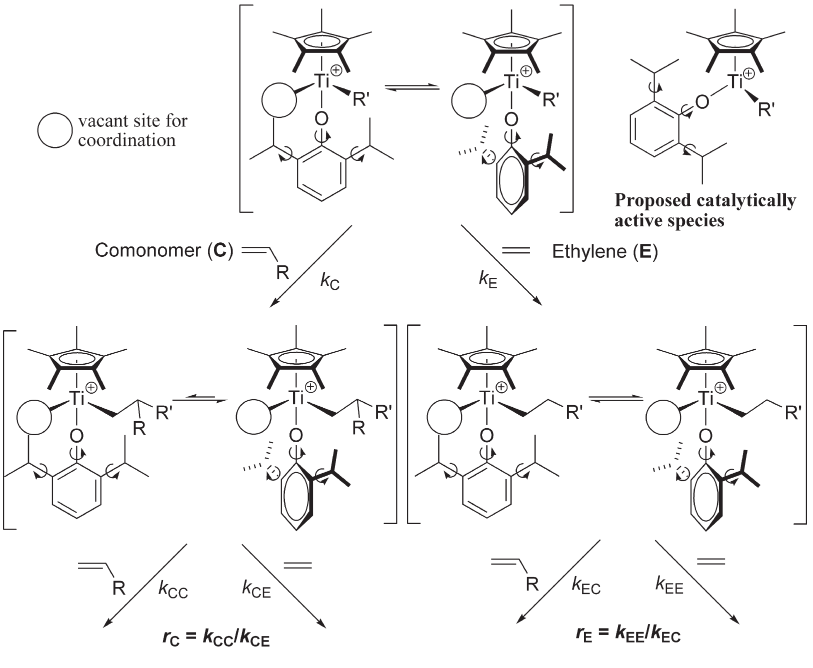


Table 4. Copolymerizations of Ethylene with 3-Methyl-1-pentene (3M1P), 4,4-Dimethyl-1-pentene (NHEP) and 3,3-Dimethyl-1-butene (NHEX) by $Cp^*TiCl_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ (1), $CpTiCl_2(N{=}C^tBu_2)$ (2), and $[Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$ (2) Catalyst Systems with MAO[a]

run	complex (amount/μmol)	ethylene/atm	comonomer (concn/M)	yield/mg	activity[b]	M_n[c] × 10^{-4}	M_w/M_n[c]	content[d]/mol %
28	**1** (0.05)	6	3M1P (1.32)	290	34800	51.2	2.29	14.4
29	**1** (0.05)	6	3M1P (2.64)	175	21000	37.9	2.52	23.5
9	**1** (0.02)	6	4M1P (1.32)	278	83400	23.3	1.94	31.4
30[e,f]	**1** (0.07)	5	HEX (1.45)	1267	181000	16.2	1.82	37.3
31	**1** (0.10)	6	NHEP (1.16)	193	11600	7.66	1.92	20.3
32	**1** (0.20)	6	NHEX (1.29)	471	14100	15.5	2.00	trace
33[e]	**2** (0.05)	6	3M1P (1.32)	112	22400	113	2.18	5.9
34	**2** (0.05)	6	3M1P (2.64)	157	18800	92.0	2.79	10.1
20	**2** (0.01)	6	4M1P (1.32)	162	97200	81.2	1.99	21.6
35[g]	**2** (0.01)	6	HEX (1.00)	190	114000	70.4	2.40	26.9
36[e]	**2** (0.10)	6	NHEP (1.16)	340	34000	53.3	2.15	10.5
37	**2** (0.20)	6	NHEX (1.29)	261	7830	71.1	1.94	trace
38	**4** (1.00)	6	3M1P (1.32)	355	2130	23.0	1.99	2.4
39	**4** (1.00)	6	3M1P (2.64)	607	3640	19.6	2.10	3.0
40	**4** (0.50)	6	NHEP (1.16)	387	4640	6.54	2.34	25.2
41	**4** (0.25)	6	NHEX (1.29)	126	3020	32.0	2.00	trace

[a] Conditions: toluene and comonomer total 30 mL, dried MAO (prepared by removing toluene and $AlMe_3$ from the ordinary MAO) 3.0 mmol, 25 °C, 10 min. [b] Activity = kg-polymer/mol-Ti·h. [c] GPC data in *o*-dichlorobenzene vs polystyrene standards. [d] Comonomer contents estimated by ^{13}C NMR spectra (^1H NMR spectra for NHEX). [e] Polymerization for 6 min. [f] Cited from ref 11b [conditions: toluene and 1-hexene (HEX) total 55 mL]. [g] Cited from ref 11c [conditions: toluene and 1-hexene (HEX) total 40 mL].

NHEP by the Cp-ketimide analogue (**2**) also proceeded with moderate catalytic activities to afford the copolymers with unimodal molecular weight distributions (runs 33, 34, and 36), whereas the copolymerization with NHEX afforded polymer containing negligible amount of NHEX (run 37), as reported previously.[24b] The NHEP content in the copolymer by **2** was lower than that prepared by **1** under the same conditions [NHEP content: 20.3 mol % by **1** (run 31) vs 10.5 mol % by **2** (run 36); ethylene 6 atm, NHEP 1.16 M], suggesting that the similar effect observed in the ethylene/4M1P copolymerization plays a role, as described below. The ethylene copolymerizations with 3M1P, NHEP by CGC (**4**) also afforded the copolymers (runs 38−40); however, the observed catalytic activities were lower than those by **1**,**2** under the same conditions.

On the basis of the above copolymerization results, the 3M1P contents in the resultant copolymers prepared by **1**,**2**,**4**−MAO catalyst systems increased in the order (conditions: ethylene 6 atm, 3M1P 2.64 M): 23.5 mol % (by **1**, run 29) ≫ 10.1 (by **2**, run 34) > 3.0 (by **4**, run 39). The results clearly indicate that **1** should be more suited as catalyst precursor than **2** and **4** for the efficient 3M1P incorporation. Importantly, efficient synthesis of high molecular weight poly(ethylene-*co*-3M1P)s by **1** should be noteworthy, because, as shown in the results by **4** as well as on the basis of previous results in the copolymerizatioin with 3-methyl-1-butene (3M1B),[26b] efficient synthesis of the copolymers especially with high comonomer content by ordinary metallocenes seemed very difficult even if the copolymerizations were conducted under higher comonomer/ethylene molar ratios,[31] because both the catalytic activities and M_n values in the copolymers decreased at higher comonomer (3M1B) concentration conditions.[26b] In this sense, as demonstrated previously in the copolymerization of ethylene with 2-methyl-1-pentene,[12] **1** should be emphasized as the promising catalyst precursor for the efficient copolymerization of ethylene with these kinds of (sterically bulky) α-olefins.

Figure 1 shows selected ^{13}C NMR spectra of poly(ethylene-*co*-3M1P)s prepared by **1**,**4** − MAO catalysts systems.[28] All resonances in the copolymer could be assigned by comparison of the spectra with different 3M1P contents as well as based on the dept analysis.[28] In addition to resonances ascribed to the isolated 3M1P incorporation, resonances ascribed to the alternating 3M1P incorporation were also seen in the copolymer prepared by **1**; resonances due to the repeated 3M1P insertion were also seen in small amount. In contrast, the spectrum for the copolymer prepared by **4** only showed resonances ascribed to the isolated 3M1P inserted unit. Figure 2 also shows selected ^{13}C NMR spectra of poly(ethylene-*co*-NHEP)s prepared by **1**,**2**−MAO catalyst systems,[28] and all resonances in the copolymer could also be assigned by comparison of the spectra with different NHEP contents as well as based on the dept analysis.[28] Similarly, resonances ascribed to alternating NHEP incorporation in addition to the resonances due to the isolated NHEP incorporation were also observed in the spectrum for the copolymer prepared by **1**.

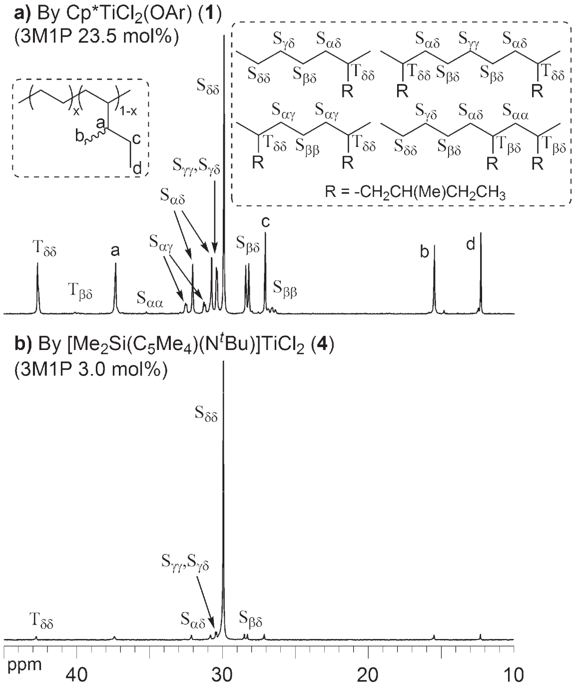


Figure 1. ^{13}C NMR spectra (in C_6D_6/1,2,4-trichlorobenzene at 110 °C) for poly(ethylene-*co*-3M1P)s prepared by a) $Cp^*TiCl_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ (**1**, run 29, 3M1P 23.5 mol %) or b) $[Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$ (**4**, run 39, 3M1P 3.0 mol %) catalyst systems with MAO (3M1P = 3-methyl-1-pentene).[28]

Table 5 summarizes monomer sequence (triad and dyad) distributions estimated on the basis of ^{13}C NMR spectra of poly(ethylene-*co*-3M1P)s, poly(ethylene-*co*-NHEP)s.[28]

The copolymerization results with 4M1P, 1-hexene (HEX) were also added for comparison. The r_E values by **1** in the ethylene/3M1P copolymerization (8.47, 8.73) were higher than those in the copolymerizations with 4M1P (2.75), HEX (2.70), NHEP (4.97); the fact should be thus explained as due to the steric bulk of substituent (R in CH_2=CHR). Note that these r_E values (8.47, 8.73) were, in fact, much smaller than those by the Cp-ketimide analogue (**2**, 28.3, run 34) as well as by CGC (**4**, 75, 92).[32] The fact clearly indicates that **1** should be suited as the distinct catalyst precursors for the efficient copolymerization with bulky (γ-branched) olefins, as also demonstrated previously in the copolymerization with vinylcyclohexane.[18]

The r_E value by **4** in the copolymerization with NHEP (4.57, run 40) was close to or somewhat smaller than that by **1** (4.97, run 31), although the r_E value by **4** in the copolymerization with 3M1P was much larger than that by **1**. The NHEP incorporation by **4** was random (r_Er_C = 0.98), whereas NHEP incorporation by **1** was rather alternating (r_Er_C = 0.43); this suggests that **4** should be suited as the catalyst precursor for synthesis of the copolymer with high NHEP content, although the activity by **4** was somewhat lower than that by **1**. As summarized in Scheme 4 (shown below), the r_E values by **2** were strongly affected by the substituent in the δ-position compared to **1**,**4**, whereas the values by CGC (**4**) were also affected by the substituent in the γ-position rather than the δ-position compared to the nonbridged half-titanocenes (**1**, **2**). The ρ values by **2** were also somewhat affected by the substituent in the δ-position, whereas these values by **1** and **4** were not strongly affected by the substituents. Although we do not have clear firm explanations for the observed facts (difference), the information obtained here should be highly promising for designing efficient catalyst for precise polymerization, especially copolymerization of ethylene with bulky α-olefins in a efficient manner.

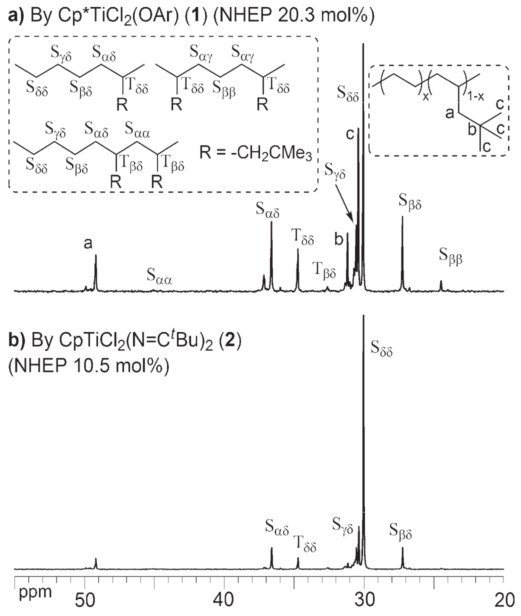


Figure 2. ^{13}C NMR spectra (in C_6D_6/1,2,4-trichlorobenzene at 110 °C) for poly(ethylene-*co*-NHEP)s prepared by a) Cp*$TiCl_2$(O-2,6-$^i Pr_2C_6H_3$) (**1**, run 31, NHEP 20.3 mol %) or b) $CpTiCl_2$(N=$C^t Bu_2$) (**2**, run 36, NHEP 10.5 mol %) catalyst systems with MAO (NHEP = 4,4-dimethyl-1-pentene).[28]

2. Copolymerization of Ethylene with 1-Dodecene (DD), and 1-Hexadecene (HD) Using Cp*$TiCl_2$(O-2,6-$^i Pr_2C_6H_3$), $CpTiCl_2$(N=$C^t Bu_2$), [$Me_2Si(C_5Me_4)(N^t Bu)$]$TiCl_2$, and Cp_2ZrCl_2−MAO Catalyst Systems. As described above, we have demonstrated that both structural features of the catalyst and steric bulk in the comonomer influence the monomer reactivity (coordination and insertion) in the copolymerization of ethylene with α-olefin containing various substituent (R in CH_2=CHR); the Cp*−aryloxo analogue (**1**) showed much better 3M1P incorporation than CGC (**4**) in the copolymerization. In order to explore the effect of linear branching toward the monomer reactivity in the copolymerization, we conducted copolymerization of ethylene with 1-dodecene (DD), and 1-hexadecene (HD) using Cp*$TiCl_2$(O-2,6-$^i Pr_2C_6H_3$) (**1**), $CpTiCl_2$(N=$C^t Bu_2$) (**2**), [$Me_2Si(C_5Me_4)(N^t Bu)$]$TiCl_2$ (**4**), Cp_2ZrCl_2 (**5**) catalyst systems with MAO. The results are summarized in Table 6.[28]

The copolymerizations of ethylene with DD, HD by both **1** and **2** proceeded with remarkable catalytic activities affording high molecular weight copolymers with unimodal molecular weight distributions in all cases. The apparent catalytic activities calculated based on the polymer yields by **2** increased upon increasing the comonomer concentration (runs 47 and 49, runs 56 and 58), whereas the opposite trend

Table 5. Monomer Sequence Distributions of Poly(ethylene-*co*-3-methyl-1-pentene)s, Poly(ethylene-*co*-4,4-dimethyl-1-pentene)s Prepared by Cp*$TiCl_2$(O-2,6-$^i Pr_2C_6H_3$) (1), $CpTiCl_2$(*N*=$C^t Bu_2$) (2), and [$Me_2Si(C_5Me_4)(N^t Bu)$]$TiCl_2$ (4) Catalyst Systems with MAO[a]

					triad sequence distribution[d] (%)					dyads[e] (%)						
run	catal	comonomer 3M1P or NHEP	[comonomer]/[E][b]	comonomer[c] content/ mol %	EEE	EEC + CEE	CEC	ECE	CCE + ECC	CCC	EE	EC + CE	CC	r_E[f]	r_C[f]	r_Er_C[g]	ρ[h]
28	**1**	3M1P	1.81	14.4	57.5	23.9	4.2	13.4	0.3	0.7	69.4	29.7	0.9	8.47	0.03	0.27	0.83
29	**1**	3M1P	3.62	23.5	38.0	30.5	8.0	20.4	1.3	1.8	53.3	44.3	2.5	8.73	0.03	0.27	0.81
31	**1**	NHEP	1.60	21.5	45.1	28.3	5.1	17.1	3.5	0.9	59.2	38.1	2.7	4.97	0.09	0.43	0.89
9	**1**	4M1P	1.81	31.4	36.7	8.7	23.2	22.7	7.7	1.0	41.0	54.1	4.9	2.75	0.10	0.27	0.80
30[i]	**1**	HEX	2.39	37.4	18.9	29.1	14.6	23.9	11.8	1.7	33.5	58.9	7.6	2.70	0.11	0.29	0.79
34	**2**	3M1P	3.62	10.1	69.9	17.7	2.2	8.7	0.9	0.6	78.8	20.2	1.0	28.3	0.03	0.80	0.90
36	**2**	NHEP	1.60	10.6	72.8	15.6	1.0	7.7	2.8	0.1	80.6	18.0	1.4	14.3	0.10	1.48	1.05
20	**2**	4M1P	1.81	21.6	55.5	4.8	20.7	12.9	5.3	0.8	63.0	33.7	3.3	6.77	0.11	0.73	1.01
35[j]	**2**	HEX	2.06	26.9	34.5	30.7	7.9	20.5	5.2	1.2	49.9	46.4	3.8	4.5	0.08	0.35	0.85
38	**4**	3M1P	1.81	2.4	93.3	4.1	0.2	2.4	trace	trace	95.4	4.6	trace	75			(1.02)
39	**4**	3M1P	3.62	3.0	89.2	7.1	0.7	3.0	trace	trace	92.7	7.3	trace	92			(0.80)
40	**4**	NHEP	1.60	25.2	41.3	27.3	6.1	12.7	11.9	0.7	55.0	38.4	6.6	4.57	0.21	0.98	0.98

[a] For detailed polymerization conditions, see Table 4, *C* = comonomer [3-methyl-1-pentene (3M1P) or 4,4-dimethyl-1-pentene (NHEP)]. [b] Initial molar ratio of [3-methyl-1-pentene (3M1P) or 4,4-dimethyl-1-pentene (NHEP)]/[ethylene] in the reaction mixture. [c] Comonomer contents in copolymer estimated by ^{13}C NMR spectra. [d] Calculated by ^{13}C NMR spectra, E = ethylene, C = comonomer [3-methyl-1-pentene (3M1P) or 4,4-dimethyl-1-pentene (NHEP)]. [e] $[EE] = [EEE] + {}^1/_2[EEC + CEE]$, $[EC] = [CEC] + [ECE] + {}^1/_2\{[EEC + CEE] + [CCE + ECC]\}$, $[CC] = [CCC] + {}^1/_2[CCE + ECC]$. [f] $r_E = [C]_0/[E]_0 \times 2[EE]/[EC + CE]$; $r_C = [E]_0/[C]_0 \times 2[CC]/[EC + CE]$. [g] $r_Er_C = 4[EE][CC]/[EC + CE]^2$. [h] $\rho = 2[E][C]/[EC]$. [i] Cited from ref 11b. [j] Cited from ref 11c.

was observed in the copolymerization if **1** was used the catalyst precursor under the same conditions (runs 43 and 46, runs 53 and 55). The observed activities by **1**,**2** were much higher than CGC (**4**) under the same conditions. The DD/HD contents in the resultant copolymers increased in the order (conditions: ex. ethylene 6 atm, HD 1.16 M): **4** (23.9 mol %, run 60) > **1** (19.8 mol %, run 55) > **2** (18.8 mol %, run 58). The significant differences in the efficiencies toward the comonomer incorporations by **1**, **2**, and **4** were not seen under these conditions, although the M_n values in the resultant copolymers prepared by **2** were much higher than those by **1** and **4**. In contrast, the copolymerizations using Cp_2ZrCl_2 (**5**)−MAO afforded the copolymers with significantly low DD/HD contents. Moreover, no significant differences in the activity and the comonomer incorporation were observed if the copolymerization was conducted in the presence of the Cp*−aryloxo−dimethyl analogue (**1′**)−borate cocatalyst system in place of the **1**−MAO catalyst system (runs 43, 44). These results clearly indicate that both **1** and **2** should be efficient catalyst precursors for copolymerization of ethylene with higher α-olefins.

Table 7 summarizes monomer sequence (triad and dyad) distributions estimated on the basis of ^{13}C NMR spectra of poly(ethylene-*co*-DD)s, poly(ethylene-*co*-HD)s.[28] As

Scheme 4

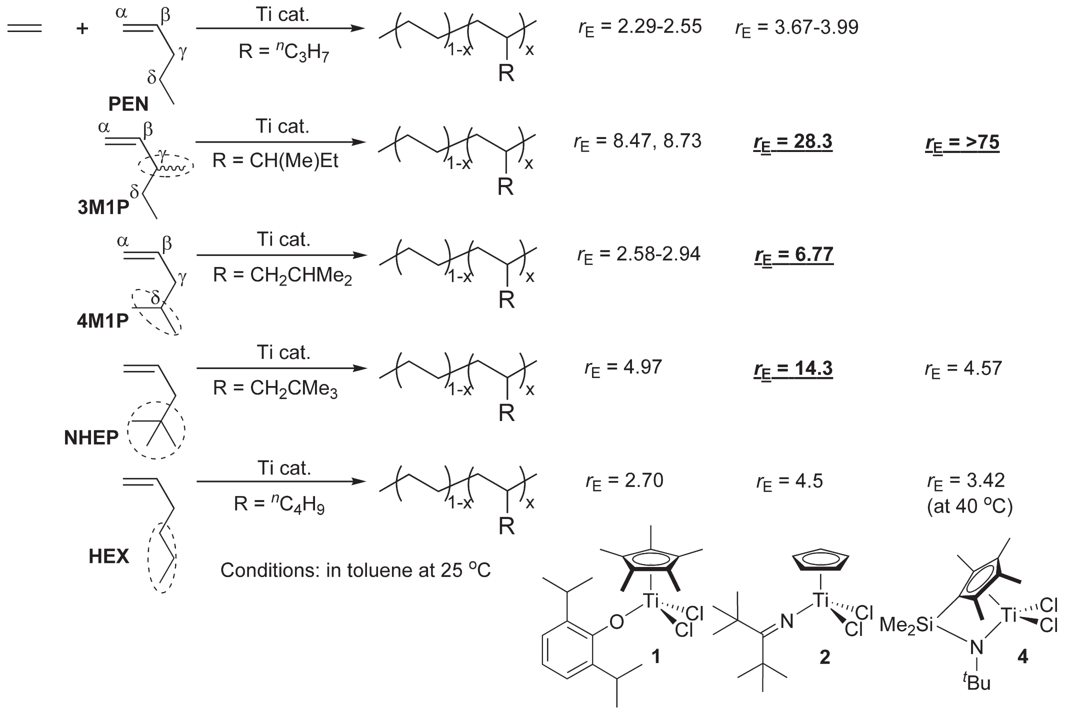


Table 6. Copolymerizations of Ethylene with 1-Dodecene (DD) or 1-Hexadecene (HD) by $Cp^*TiCl_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ (1), $Cp^*TiMe_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ (1′), $CpTiCl_2(N{=}C^tBu_2)$ (2), $[Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$ (4), and Cp_2ZrCl_2 (5) Cocatalyst Systems[a]

			comonomer						
run	complex (amount/μmol)	ethylene/atm	DD or HD	concn/M	yield/mg	activity[b]	M_n[c] × 10^{-4}	M_w/M_n[c]	content[d]/mol %
42	**1** (0.01)	8	DD	0.75	694	416000	18.6	1.93	14.8
43	**1** (0.01)	6	DD	0.75	384	230000	18.7	1.99	19.2
44[e]	**1′** (0.01)	6	DD	0.75	368	221000	23.2	2.07	19.4
45	**1** (0.01)	4	DD	0.75	223	134000	18.0	1.93	22.9
46	**1** (0.01)	6	DD	1.50	335	201000	15.8	2.03	27.8
47	**2** (0.01)	6	DD	0.75	205	123000	48.4	1.97	15.5
48	**2** (0.01)	4	DD	0.75	158	95000	51.9	1.86	19.9
49	**2** (0.01)	6	DD	1.50	305	183000	61.6	1.85	22.6
50	**4** (0.1)	6	DD	0.75	413	24800	39.1	2.09	19.2
51	**4** (0.1)	6	DD	1.50	245	15600	31.2	2.08	33.1
52	**5** (0.01)	6	DD	0.75	301	181000	56.2	1.99	2.0
53	**1** (0.01)	6	HD	0.58	456	274000	21.7	2.08	11.9
54	**1** (0.01)	4	HD	0.58	235	141000	16.5	1.99	15.4
55	**1** (0.01)	6	HD	1.16	174	104000	23.3	2.02	19.8
56	**2** (0.01)	6	HD	0.58	192	115000	63.7	1.96	10.9
57	**2** (0.01)	4	HD	0.58	111	66600	87.1	1.95	14.7
58	**2** (0.01)	6	HD	1.16	296	178000	86.0	1.87	18.8
59	**4** (0.1)	6	HD	0.58	440	26400	42.3	2.13	13.8
60	**4** (0.1)	6	HD	1.16	286	17200	34.0	2.09	23.9
61	**5** (0.01)	6	HD	0.58	310	186000	68.8	1.82	1.6

[a] Conditions: toluene and DD or HD total 30 mL, dried MAO (prepared by removing toluene and $AlMe_3$ from the ordinary MAO) 3.0 mmol, 25 °C, 10 min. [b] Activity = kg-polymer/mol-Ti·h. [c] GPC data in *o*-dichlorobenzene vs polystyrene standards. [d] Comonomer contents estimated by ^{13}C NMR spectra. [e] Cocatalyst is $Al^iBu_3/[Ph_3C]^+[B(C_6F_5)_4]^-$, [Ti]/[B]/[Al] = 1/3/500.

Table 7. Monomer sequence distribution of poly(ethylene-*co*-1-dodecene)s, poly(ethylene-*co*-1-hexadecene)s prepared by by Cp*TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (1), CpTiCl$_2$(N=C^{t}Bu$_2$) (2), [Me$_2$Si(C$_5$Me$_4$)(N^{t}Bu)]TiCl$_2$ (4), Cp$_2$ZrCl$_2$ (5) − MAO catalyst systems.[a]

					triad sequence distribution[d] (%)						dyads[e] (%)						
run	catal	DD or HD	[comonomer]/[E][b]	comonomer content[c]/mol %	EEE	EEC + CEE	CEC	ECE	CCE + ECC	CCC	EE	EC + CE	CC	r_E[f]	r_C[f]	r_Er_C[g]	ρ[h]
42	**1**	DD	0.77	14.8	56.8	26.0	2.4	12.7	2.1	trace	69.8	29.1	1.1	3.71	0.09	0.35	0.87
43	**1**	DD	1.03	19.2	48.2	30.1	2.5	15.8	3.4	trace	63.3	35.1	1.6	3.72	0.09	0.35	0.88
45	**1**	DD	1.55	22.9	39.0	30.7	7.3	17.4	5.2	0.4	54.4	42.7	2.9	3.95	0.09	0.35	0.83
46	**1**	DD	2.06	27.8	31.2	30.6	10.4	20.0	6.4	1.4	46.5	49.0	4.5	3.92	0.09	0.35	0.82
53	**1**	HD	0.80	11.9	65.5	21.0	1.7	10.5	1.3	trace	76.0	23.4	0.6	5.20	0.07	0.36	0.90
54	**1**	HD	1.20	15.4	53.7	27.2	3.7	12.8	2.6	trace	67.3	31.4	1.3	5.15	0.07	0.36	0.83
55	**1**	HD	1.60	19.8	47.0	27.4	5.7	16.0	3.7	0.2	60.7	37.3	2.0	5.22	0.07	0.35	0.85
47	**2**	DD	1.03	15.5	57.4	26.2	0.9	13.3	2.0	0.2	70.6	28.2	1.2	5.16	0.08	0.43	0.93
48	**2**	DD	1.55	19.9	45.4	31.9	2.8	15.8	3.2	0.8	61.4	36.2	2.4	5.26	0.09	0.46	0.88
49	**2**	DD	2.06	22.6	39.1	31.8	6.5	16.4	4.9	1.3	55.0	41.3	3.7	5.50	0.09	0.48	0.85
56	**2**	HD	0.80	10.9	68.9	20.0	0.2	9.6	1.3	trace	79.0	20.4	0.6	6.18	0.08	0.48	0.95
57	**2**	HD	1.20	14.7	58.9	25.5	0.9	12.4	2.3	trace	71.7	27.1	1.2	6.34	0.07	0.46	0.93
58	**2**	HD	1.60	18.8	52.6	23.7	3.6	16.2	3.9	trace	64.4	33.6	2.0	6.14	0.07	0.45	0.91
50	**4**	DD	1.03	19.2	49.8	30.8	3.7	9.9	4.6	1.2	65.2	31.3	3.5	4.31	0.22	0.94	0.99
51	**4**	DD	2.06	33.1	29.2	31.8	10.0	12.1	11.3	5.6	45.0	43.7	11.3	4.26	0.25	1.06	1.01
59	**4**	HD	0.80	13.8	63.3	20.1	2.7	9.8	4.0	0.1	73.3	24.6	2.1	4.78	0.21	1.02	0.97
60	**4**	HD	1.60	23.9	44.1	24.7	7.3	13.4	9.0	1.5	56.4	37.6	6.0	4.80	0.20	0.96	0.97
52	**5**	DD	1.03	2.0	93.8	4.3	trace	1.9	trace	trace	95.7	4.3	trace	49			0.91
61	**5**	HD	0.80	1.6	95.6	2.8	trace	1.6	trace	trace	97.0	3.0	trace	51			1.05

[a] Detailed polymerization conditions, see Table 6, C = comonomer [1-dodecene (DD) or 1-hexadecene (HD)]. [b] Initial molar ratio of [1-hexadecene (HD) or 1-dodecene (DD)]/[ethylene] in the reaction mixture. [c] 1-hexadecene contents in copolymer estimated by ^{13}C NMR spectra. [d] Calculated by ^{13}C NMR spectra, E = ethylene, C = comonomer [1-dodecene (DD) or 1-hexadecene (HD)]. [e] $[EE] = [EEE] + {}^1/_2[EEC + CEE], [EC] = [CEC] + [ECE] + {}^1/_2\{[EEC + CEE] + [CCE + ECC]\}, [CC] = [CCC] + {}^1/_2[CCE + ECC]$. [f] $r_E = [C]_0/[E]_0 \times 2[EE]/[EC + CE], r_C = [E]_0/[C]_0 \times 2[CC]/[EC + CE]$. [g] $r_Er_C = 4[EE][CC]/[EC + CE]^2$. [h] $\rho = 2[E][C]/[EC]$.

reported in the ethylene/1-hexene copolymerization,[11,11] the resultant copolymers prepared by **1** possessed relatively higher percentage of ECE, and EC + CE sequences (E = ethylene, C = comonomer such as DD, HD) and the r_Er_C values by **1** calculated from the dyads were small (0.35−0.36), and the r_Er_C values by **2** were also relatively small (0.43−0.48); the ρ values by **1**,**2** were slightly smaller than 1 (0.87−0.93). In contrast, both the r_Er_C values and ρ values by CGC, (**4**) were ca. 1.0, clearly indicating that these copolymerizations by **4** proceed in a random manner (comonomer incorporations are random). These results should be unique contrast for using this type of catalyst precursors for the ethylene copolymerization. The results also suggest that **4** would be more suited than **1** and **2** to obtain the copolymers with high comonomer contents, although the activities by **4** were much lower than those by **1** and **2**. The r_E values in the ethylene/DD copolymerization decreased in the order: **5** (49, run 52) > **2** (5.15−5.50, runs 47−49) > **4** (4.26,4.31, runs 50−51) > **1** (3.71−3.95, runs 42−46), whereas the order was different in the ethylene/HD copolymerization: **5** (51, run 61) > **2** (6.14−6.34, runs 56−58) > **1** (5.15−5.22, runs 53−55) > **4** (4.78,4.80, runs 59−60). The results also suggest that degree of influence of the linear long chain branching toward the r_E values were dependent upon the catalyst (ligand set) employed.

Concluding Remarks

We have explored copolymerization of ethylene with substituted pentenes [1-pentene (PEN), 4-methyl-1-pentene (4M1P), 3-methyl-1-pentene (3M1P), 4,4-dimethyl-1-pentene (NHEP)] using Cp*TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (**1**), CpTiCl$_2$(N=C^{t}Bu$_2$) (**2**) catalyst systems with MAO, and the constrained geometry catalyst (CGC), [Me$_2$Si(C$_5$Me$_4$)(N^{t}Bu)]TiCl$_2$ (**4**), was also used for comparison. The copolymerizations with 1-dodecene (DD), 1-hexadecene (HD) using **1**, **2**, **4** and Cp$_2$ZrCl$_2$ (**5**) catalyst systems with MAO were also conducted to explore the influence of linear branching toward the monomer reactivity (r_E values in the copolymerization). Table 8 summarizes r_E, r_C (E = ethylene, C = comonomer) and r_Er_C values in the copolymerizations by the Cp*-aryloxo analogue (**1**), the Cp−ketimide analogue (**2**) and CGC (**4**) based on the experimental results (in toluene at 25 °C). Note that r_Er_C values by **1** in the copolymerization were small in all cases, suggesting that the comonomer incorporations were rather alternating, whereas the copolymerization by **4** proceeded in a random manner (comonomer incorporations were random, r_Er_C = ca. 1) except the copolymerization with 3M1P. The observed differences also well emphasize unique characteristics for using nonbridged half-titanocenes for precise olefin copolymerization, as demonstrated previously.[8,11,11]

The r_E values in the copolymerization of linear α-olefins by **1** decreased in the order: HD (5.22) > DD (3.92) > HEX (2.70) > PEN (r_E = 2.50). The similar trend was seen in both **2** and **4**, but the r_E value in the copolymerization with HD by **4** (4.78, 4.80) was smaller than that by **1** (5.15, 5.22), suggesting that the effect (toward the r_E values) was also dependent upon the nature of the catalysts (ligand set) employed. The fact also indicates that **4** showed more efficient comonomer incorporations than **1**,**2**, although the observed catalytic activities by **4** were much lower than those by **1**. Since the observed difference in the r_E values are not significant, **1** should be considered as the suited catalyst precursor in terms of both the activity and the comonomer (DD, HD) incorporation in these copolymerizations.

Note that the Cp*-aryoloxo analogue (**1**) exhibited remarkable both catalytic activities and notable 3M1P incorporation in the ethylene/3M1P copolymerization, and the r_E value (8.73) was much smaller than that by CGC (**4**, 92) as well as by the Cp−ketimide analogue (**2**, 28.3). The results clearly indicate that **1** should be suited as the catalyst precursor for efficient copolymerization of ethylene with branched α-olefins, as also demonstrated previously by the copolymerization with 2-methyl-1-pentene[12] and vinylcyclohexane.[18] Although **1** and **4** showed efficient NHEP incorporations in the ethylene/NHEP copolymerization, **2** showed less efficient NHEP incorporation; the rather large r_E values (6.77) compared to **1** (2.58−2.94) were also obtained in the copolymerization with 4M1P. The results suggest that the monomer reactivity by **2** was influenced by the substituent in the δ-position (in addition to the substituent in the γ-position),

Table 8. Summary of r_E and r_C (c = comonomer) values in copolymerization of ethylene with various olefins ($CH_2{=}CHR$) by $Cp^*TiCl_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ (1), $CpTiCl_2(N{=}C^tBu_2)$ (2), $[Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$ (4) − MAO catalyst systems (in toluene at 25 °C).[a]

run	catal	comonomer	R	content[b]/mol %	r_E	r_C	r_Er_C	ρ
5	$Cp^*TiCl_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ (**1**)	1-pentene (PEN)	$n\text{-}C_3H_7$	31.2	2.50	0.11	0.27	0.81
30[c]	$Cp^*TiCl_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ (**1**)	1-hexene (HEX)	$n\text{-}C_4H_9$	37.4	2.70	0.11	0.29	0.79
9	$Cp^*TiCl_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ (**1**)	4-methyl-1-pentene (4M1P)	$\text{-}CH_2CH(CH_3)_2$	31.4	2.75	0.10	0.27	0.80
29	$Cp^*TiCl_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ (**1**)	3-methyl-1-pentene (3M1P)	$\text{-}CH(Me)C_2H_5$	23.5	8.73	0.03	0.27	0.81
31	$Cp^*TiCl_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ (**1**)	4,4-dimethyl-1-pentene (NHEP)	$\text{-}CH_2CMe_3$	21.5	4.97	0.09	0.43	0.89
46	$Cp^*TiCl_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ (**1**)	1-dodecene (DD)	$n\text{-}C_{10}H_{21}$	27.8	3.92	0.09	0.35	0.82
55	$Cp^*TiCl_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ (**1**)	1-hexadecene (HD)	$n\text{-}C_{14}H_{29}$	19.8	5.22	0.07	0.35	0.85
15	$CpTiCl_2(N{=}C^tBu_2)$ (**2**)	1-pentene (PEN)	$n\text{-}C_3H_7$	29.1	3.97	0.09	0.35	0.84
35[d]	$CpTiCl_2(N{=}C^tBu_2)$ (**2**)	1-hexene (HEX)	$n\text{-}C_4H_9$	26.9	4.5	0.08	0.35	0.85
20	$CpTiCl_2(N{=}C^tBu_2)$ (**2**)	4-methyl-1-pentene (4M1P)	$\text{-}CH_2CH(CH_3)_2$	21.6	6.77	0.11	0.73	1.01
34	$CpTiCl_2(N{=}C^tBu_2)$ (**2**)	3-methyl-1-pentene (3M1P)	$\text{-}CH(Me)C_2H_5$	10.1	28.3	0.03	0.80	0.90
36	$CpTiCl_2(N{=}C^tBu_2)$ (**2**)	4,4-diemthyl-1-pentene (NHEP)	$\text{-}CH_2CMe_3$	10.6	14.3	0.10	1.48	1.05
48	$CpTiCl_2(N{=}C^tBu_2)$ (**2**)	1-dodecene (DD)	$n\text{-}C_{10}H_{21}$	19.9	5.26	0.09	0.46	0.88
58	$CpTiCl_2(N{=}C^tBu_2)$ (**2**)	1-hexadecene (HD)	$n\text{-}C_{14}H_{29}$	18.8	6.14	0.07	0.45	0.91
62[c]	$[Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$ (**4**)	1-hexene (HEX)	$n\text{-}C_4H_9$	30.0	3.42	0.29	0.99	1.01
39	$[Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$ (**4**)	3-methyl-1-pentene (3M1P)	$\text{-}CH(Me)C_2H_5$	3.0	92	–	–	–
40	$[Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$ (**4**)	4,4-diemthyl-1-pentene (NHEP)	$\text{-}CH_2CMe_3$	25.2	4.57	0.21	0.98	0.98
50	$[Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$ (**4**)	1-dodecene (DD)	$n\text{-}C_{10}H_{21}$	19.2	4.31	0.22	0.94	0.99
60	$[Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$ (**4**)	1-hexadecene (HD)	$n\text{-}C_{14}H_{29}$	23.9	4.80	0.20	0.96	0.97

[a] Data cited from Tables 3,5, and 7. [b] Comonomer contentss (mol %) estimated by ^{13}C NMR spectra. [c] Cited from ref 11b (at 40 °C). [d] Cited from ref 11c.

whereas the monomer reactivity by **4** was more influenced by the substituent in the γ-position rather than the δ-position (Scheme 4).

The results through this research clearly indicate that the monomer reactivities (r_E values) are strongly influenced not only by the substituent in the olefins, but also by the (both electronic and steric) nature of the catalytically active species (structure, and ligand set employed). The information here should be potentially important for designing more effective catalyst for efficient, precise olefin polymerization, especially directed toward synthesis of new polymers produced by incorporation of new comonomers.

Experimental Section

General Procedure. All experiments were carried out under nitrogen atmosphere in a Vacuum Atmospheres drybox unless otherwise specified. Anhydrous grade of toluene (Kanto Kagaku Co. Ltd.) was transferred into a bottle containing molecular sieves (mixture of 3A $^1/_{16}$ and 4A $^1/_8$, and 13X $^1/_{16}$) in the drybox, and was used without further purification. 1-Pentene (Tokyo Kasei Kogyo Co., Ltd.) and 4-methyl-1-pentene (Tokyo Kasei Kogyo Co., Ltd.), 3-methyl-1-pentene (Aldrich), 4,4-dimethyl-1-pentene (Tokyo Kasei Kogyo Co., Ltd.), 3,3-dimethyl-1-pentene (Tokyo Kasei Kogyo Co., Ltd.), 1-dodecene (Mitsubishi Chemical Co.), and 1-hexadecene (Mitsubishi Chemical Co.) of reagent grades were stored in bottles in the drybox in the presence of molecular sieves. Polymerization grade ethylene (purity > 99.9%, Sumitomo Seika Co. Ltd.) was used as received. Toluene and $AlMe_3$ in the commercially available methylaluminoxane [PMAO-S, 9.5 wt % (Al) toluene solution, Tosoh Finechem Co.] were removed under reduced pressure (at ca. 50 °C for removing toluene, $AlMe_3$, and then heated at > 100 °C for 1 h for completion) in the drybox to give white solids. $Cp^*TiCl_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ (**1**),[17] $CpTiCl_2(N{=}C^tBu)$ (**2**),[33] $({}^tBuC_5H_4)TiCl_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ (**3**),[17] and $[Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$ (CGC, **4**),[34] were prepared according to the reported procedures. Cp_2ZrCl_2 (**5**, Wako Pure Chemical. Ind., Ltd.) was used as received.

Molecular weights and molecular weight distributions for polyethylene and the copolymers were measured by gel permeation chromatography (Tosoh HLC-8121GPC/HT) with a polystyrene gel column (TSK gel GMHHR-H HT×2, 30 cm × 7.8 mm i.d.), ranging from $< 10^2$ to $< 2.8 \times 10^8$ MW) at 140 °C using *o*-dichlorobenzene containing 0.05 wt/v% 2, 6-di-*tert*-butyl-*p*-cresol as eluent. The molecular weight was calculated by a standard procedure based on the calibration with standard polystyrene samples.

All ^1H and ^{13}C NMR spectra were recorded on a JEOL JNM-LA400 spectrometer (399.65 MHz, ^1H). All deuterated NMR solvents were stored over molecular sieves under a nitrogen atmosphere, and all chemical shifts are given in ppm and are referenced to Me_4Si. ^{13}C NMR spectra for all the copolymers were recorded on a JEOL JNM-LA400 spectrometer (100.40 MHz, ^{13}C) with proton decoupling. The pulse interval was 5.2 s, the acquisition time was 0.8 s, the pulse angle was 90°, and the number of transients accumulated was ca. 8000. The analysis polymer samples were prepared by dissolving polymers in a mixed solution of 1,2,4-trichlorobenzene/benzene-d_6 (90/10 w/w), and these spectra were measured at 110 °C.

Copolymerization of Ethylene with α-Olefins. A typical procedure (Table 1, run 2) for ethylene/1-pentene copolymerization was performed as follows: the prescribed amounts of toluene (24.0 mL), 1-pentene (5.0 mL), d-MAO (174 mg, 3.0 mmol) were added into the autoclave (100 mL scale) in the drybox, and the apparatus was then purged with ethylene. The reaction mixture was then pressurized to 5 atm (total ethylene 6 atm) soon after the addition of a toluene solution (1.0 mL) containing **1** (0.02 μmol). The mixture was magnetically stirred for 10 min, the ethylene remaining was purged after the reaction upon cooling in the ice bath. The mixture was then poured into EtOH (50 mL) containing HCl (5 mL). The resultant polymer was collected on a filter paper by filtration, was adequately washed with EtOH, and was then dried *in vacuo* at 60 °C for several hours.

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Supporting Information Available: Figures showing selected ^{13}C NMR spectra for ethylene copolymers including their peak assignments described in this work. This material is available free of charge via the Internet at http://pubs.acs.org.

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(29) These copolymerizations were terminated at the initial stage, and termination with the comonomer conversion less than 10% should be very important to obtain the copolymers with uniform composition distribution.

(30) Although we have no firm *direct* confirmations concerning the rotation of the aryloxide ligands, Kang (Korea Univ.) et al. recently presented detailed study of the flexible rotation on the basis of NMR spectra and calculation results. Kim, T.-J.; Kim, S. K.; Hahn, J.-S.; Ok, M.-A.; Song, J. H.; Shin, D.-H.; Ko, J.; Minserk, C.; Mitoraj, M.; Srebro, M.; Michalak, A.; Kang, S. O. *Abstract in 102nd Korean Chemical Society National Meeting*, Jeju, Korea, October **2008**.

(31) For example, 3-methyl-1-butene (3M1B) content in the resultant copolymer in the ethylene/3M1B copolymerization was 9.9, 18.1 mol %, respectivlely, when the copolymerizations by **4** were conducted under the initial molar ratios of [3M1B]/[E] = 20, 49,

respectively,[26b] whereas 3M1P content in the copolymer was 23.5 mol % when the copolymerization by **1** was conducted under the initial molar ratio of [3M1P]/[E] = 3.62 (run 29, Table 4). The 3M1B contents were 0.2, 19.4 mol %, respectively, when the copolymerizations by [$Me_2Si(indenyl)_2$]$ZrCl_2$ were conducted under the initial molar ratio of [3M1B]/[E] = 5, 10, respectively. It is thus clear that **1** exceptionally efficient incorporates 3M1P (branched α-olefin) in the copolymerization, and should be effective for synthesis of high molecular weight copolymers with relatively high 3M1P contents.

(32) Estimation of the r_E values in the ethylene/3M1P copolymerizations by CGC (**4**, 75, 92) seemed difficult due to their low 3M1P contents. (runs 38−39, 3M1P 2.4, 3.0 mol %, respectively).

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